

4th International Conference Photonics and Information Optics, PhIO 2015, 28-30 January 2015

Effect of laser treatment on shape memory properties of TiNiCu alloy

Alexander Shelyakov^{a*}, Nikolay Sitnikov^{a,b}, Kirill Borodako^a, Alexey Menushenkov^a,
Vyacheslav Fominski^a

^aNational Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe shosse 31, Moscow 115409, Russia

^bFederal State Unitary Enterprise "Keldysh Research Center", Onezhskaya St. 8, Moscow 125438, Russia

Abstract

The work deals with the research of the effect of pulsed laser radiation ($\lambda=248$ nm) on the structure and the manifestation of the shape memory effects (SMEs) in the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy, produced by melt spinning technique. It has been revealed that the proposed method of laser treatment leads to the formation of structural amorphous-crystalline composite demonstrating the pronounced two-way SME. A dependence of the two-way SME on the number of laser radiation pulses was determined.

© 2015 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the National Research Nuclear University MEPhI (Moscow Engineering Physics Institute)

Keywords: shape memory alloys; melt-spun ribbons; laser treatment; amorphous–crystalline alloy; two-way shape memory effect.

1. Introduction

The dynamics of progress of XXI century high technologies has been governed, for the most part, by creation of radically new advanced materials meeting various demands of the society evolution. To these materials can be pertinent alloys which exhibit the shape memory effect (SME). They have found efficient applications to various fields – from medicine to space technologies [Van Humbeeck (1999), Hartl, Lagoudas (2007), Petrini, Migliavacca (2011), Shelyakov, Larin, Ivanov (2003), Sun et al. (2012)]. Meanwhile up-to-date engineering progress imposes more and more requirements for functional metallic materials. The problem becomes especially important when passing to micro- and nanosize levels, as standard material-science principles of forming structure and properties

* Corresponding author. Tel.: Tel.: +7-495-788-5699 ext. 81-69; fax: +7-499-324-2111

E-mail address: AVShelyakov@mephi.ru

become extremely inefficient and incapable of satisfying these requirements. In some researches of last years it has been revealed that the key point of obtaining new unusual properties of materials involves the production in them crucially new, previously unknown structural states, and the technique for the creation of similar structures consists in the extreme action on materials [Glezer (2012)]. The modifying treatment of the SME materials with the aid of extreme impacts (super rapid quenching from the melt, ion-plasma treatment, dynamic crystallization, laser action) provides the formation of unique structural-phase states [Shelyakov, Sitnikov, Menushenkov et al. (2011), Lagrange, Gotthardt (2003), Birnbaum et al. (2009), Wang et al. (2005)]. The treatment with concentrated energy fluxes implies simultaneous radiation, thermal and shock actions. Restructuring processes, which are evolving thereat, take place in the conditions being far from thermodynamically equilibrium; they allow it to produce materials with a unique complex of physical-mechanical characteristics including the structures with the two-way SME (TWSME) [Shelyakov, Sitnikov, Saakyan et al. (2013), Shelyakov, Sitnikov, Menushenkov et al. (2013), Shelyakov et al. (1995), Matveeva et al. (1997)]. The latter is very important because the property of reversible deformation is not intrinsic in the SME alloys. At the same time practical applications of the SME alloys, in particular, to the creation of micromechanical devices [Bellouard (2008), Nespoli et al. (2010), Shelyakov, Sitnikov, Kolledov et al. (2011), Zakharov et al. (2010), Irzhak et al. (2014), Fu et al. (2007), Freed, Aboudi (2009), Gill et al. (2002), Lagrange, Gotthardt (2003)], usually calls for reversible change of the shape in the heating-cooling cycle. In the present work the TiNiCu alloy was subjected to a combination of extreme actions – rapid quenching from the melt and the subsequent action of laser radiation. The influence of laser radiation parameters on the alloy structure and the manifestation of SMEs was considered with the outlook for creation of microdevices on its base.

2. Materials and Methods

The quasi-binary $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ (at.%) alloy was chosen as the subject of the investigation. The alloy samples were produced by the melt-spinning technique at a melt cooling rate as high as about 10^6 K/s in the form of amorphous ribbons at around 40 μm of thickness and 2 mm of width [Potapov et al. (2003), Chang et al. (2007), Morgiel et al. (2002), Menushenkov et al. (2014), Rösner et al. (1999), Park et al. (2006)].

For the formation of the TWSME through the laser radiation, the technique, schematically shown in Fig. 1, was used. The original amorphous ribbon of rectangular shape bends around a special mandrel and is fastened in this state (Fig. 1a). Then the sample is subjected to isothermal crystallization in a furnace at the temperature of 500°C during 300 sec to give it the shape memory for the bended state with the bending radius as 1.5 mm (Fig. 1a). Thereafter the sample is unbended, and the bending zone is affected by laser radiation which can give rise to the modification (amorphization) of the ribbon surface layer (Fig. 1b). As a result, a structural composite, consisting of the crystalline and amorphous layers, is formed. After the release of the sample from the mandrel and the following heating above the temperature A_f of the finish of the reverse martensitic transformation (MT) in the crystalline layer, the ribbon bends due to SME recovering the given shape and stretching the amorphous layer (Fig. 1c).

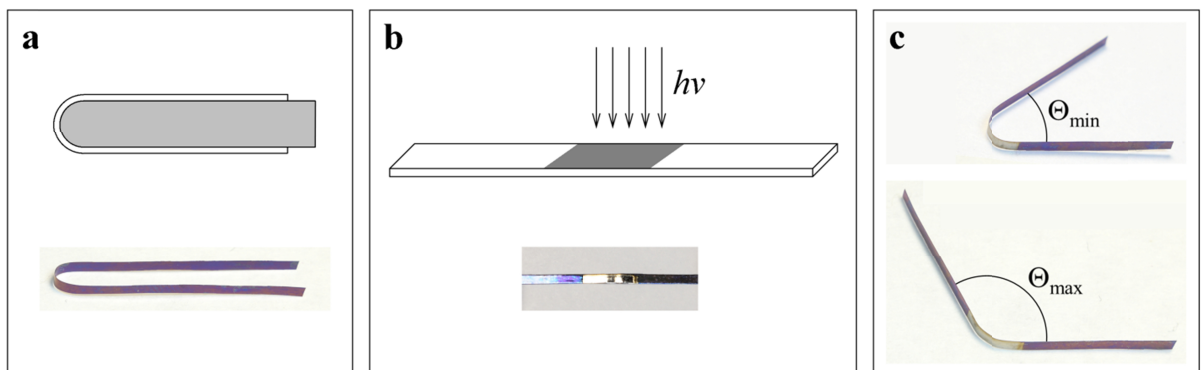


Fig. 1. Schematic representation of the technique for creating the TWSME in a SMA ribbon with laser radiation:

(a) – shape setting a ribbon, (b) – laser irradiation of a ribbon, (c) – TWSME in a ribbon.

In so doing, the sample passes to the “hot” state characterized by the angle θ_{min} . By the cooling in the process of the direct MT the amorphous layer acts as an elastic force and unbends the sample deforming the crystalline layer, and the sample changes to the “cold” state with the angle θ_{max} . Later on reversible bending deformations are happening in the heating-cooling cycle, i.e. the amorphous-crystalline composite ribbon is capable to exhibit the TWSME.

The radiation of the CL7000 series excimer laser with a KrF gas mixture (wavelength 248 nm; pulse duration 20 ns; pulse energy density 17 mJ/mm^2) was used for modification of alloy properties. In doing so, the number of laser radiation pulses was varied from 1 to 100 at a pulse repetition rate 20 Hz.

Sample preparation for the scanning electron microscopic research was carried out using metallographic sectioning equipment from the BUEHLER® Company. The final step of polishing was performed using oxygen-containing mixed suspension MASTERPOLISH with abrasive grit 50 nm ($\text{Al}_2\text{O}_3 + \text{SiO}_2$).

The microstructure of the sample was studied using the scanning electron microscope FEI Quanta 600 FEG with the field-emission cathode.

Phase compositions were determined by X-ray diffraction at room temperature on a SHIMADZU XRD-6000 vertical X-ray diffractometer with $\text{Cu}_{K\alpha}$ radiation ($\lambda_{av} = (2\lambda_{K\alpha1} + \lambda_{K\alpha2})/3 = 1.54178 \text{ \AA}$). The crystal lines were identified using ICDD PDF Release 2004 data.

3. Results and Discussion

The investigation into the influence of laser radiation parameters on the TWSME behaviour of irradiated ribbons was conducted through thermal cycling of the samples at the MT interval. For this purpose a special installation with video recording of the shape change at varying temperature was developed. On each frame the angle θ was determined with the aid of the special software. Presented in Fig. 2 are the dependences, obtained for the characteristic angles θ_{max} and θ_{min} on laser action parameters. It is seen that the increase in the number of pulses from 1 to 10 gives rise not only to the increase in the angles θ_{max} and θ_{min} , but also to that of their difference $\Delta\theta$, which is peculiar to the magnitude of the TWSME. At the same time with a growth of the number of pulses from 10 to 100 the characteristic angles θ_{max} and θ_{min} also increase, however their difference $\Delta\theta$ decreases. The character of this dependence differs essentially from the previously established correlation between the energy of a single pulse of laser radiation and the typical characteristic angles, in particular, the increase in the energy density from 1 to 20 mJ/mm^2 resulted in the growth of $\Delta\theta$ from 28 to 74 degrees. It is obvious that such a distinction is caused by a different dynamics of processes of laser radiation interaction with the sample, taking place in one case with the variation in the single pulse energy, in the other – by the variation of the number of pulses at a fixed energy.

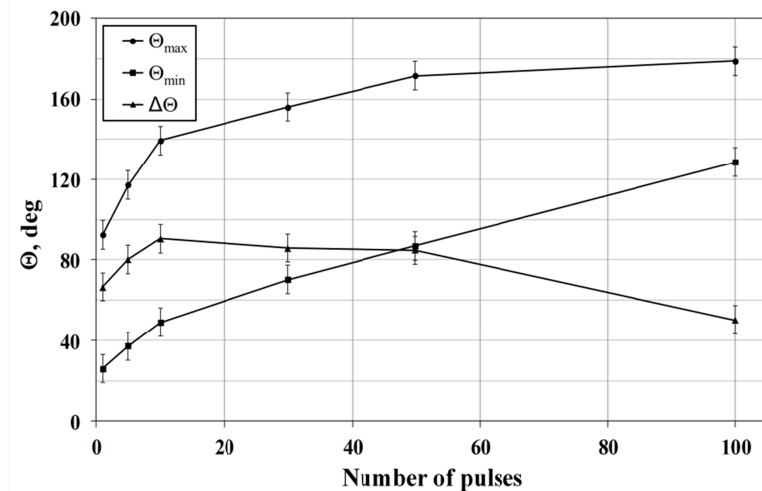


Fig. 2. The characteristic bending angles of the irradiated ribbon as a function of the number of laser radiation pulses ($E = 17 \text{ mJ/mm}^2$).

For the elucidation of reasons of the effects observed the structural investigations of the samples by means of electron microscopy and X-ray diffraction methods were carried out. Shown in Fig. 3a is the typical diffraction pattern of the original crystalline ribbon prior to its laser radiation treatment, on which reflections of the martensite phase B19 are clearly seen. The action of an even one pulse of the laser radiation leads to the decrease in the peaks of reflection of the phase B19 (Fig. 3b), which is indicative of the decrease of a fraction of the crystalline phase, most likely, due to a partial amorphization. The increase of the number of pulses to 50 leads to a further greater decrease in the intensity of reflections (Fig. 3c,d), and in the samples, treated by the laser radiation with the number of pulses more than 100, no presence of the B19-phase was discovered. This testifies that with the growth of the number of pulses, in the first place, the thickness of the modified layer grows to the quantity exceeding the depth of penetration of X-rays, and, secondly, the crystalline structure of the martensite B19-phase disintegrates at the expense of forming the modified structure containing the amorphous phase.

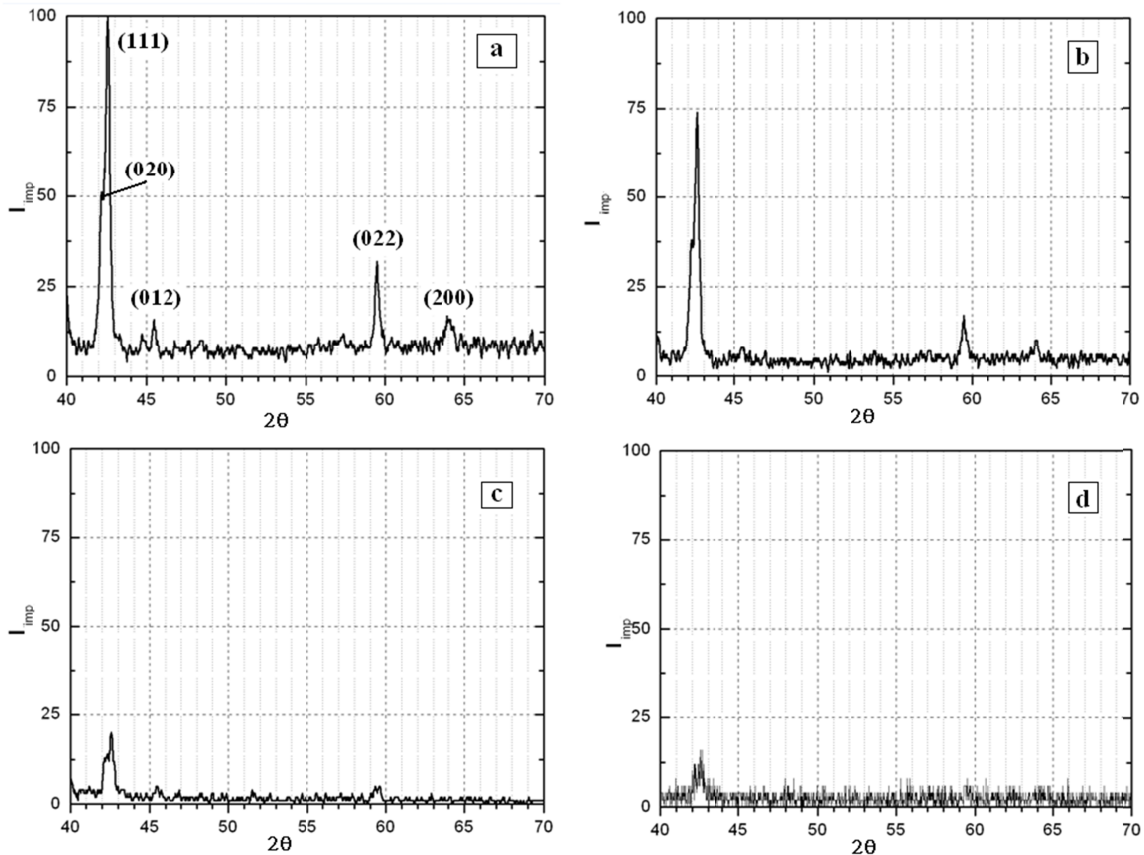


Fig. 3. X-ray diffraction patterns of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy ribbon in original crystalline state (a) and after irradiation with the different number of laser radiation pulses: 1 (b), 10 (c) and 50 (d).

Electron-microscope investigations into the samples cross-sections revealed a sharp boundary between the thin surface layer and the rest of the ribbon part (Fig. 4). In so doing, it has been ascertained that the increase in the number of pulses of laser radiation from 1 to 100 results in the growth of the surface layer thickness from 1.2 to 2.2 μm . On the basis of results of X-ray structural analysis, it may be supposed with a great certainty that this layer has the amorphous structure. However, from the pictures obtained is seen that at the great number of pulses (Fig. 4e,f) the modified layer has the much greater thickness, i.e. it includes not only a prominent surface layer, but a broad region of the ribbon differing in its structure from the original crystalline one. This confirms the above results of the X-ray investigations of the samples treated with a great number of pulses of laser radiation. It is worth noting that

the exacter determination of microstructure of the modified layer may be gained with the aid of transmission electron microscopy, which was not done because of the complexity of the preparation of samples for this experiment, but it would be a goal of further researches.

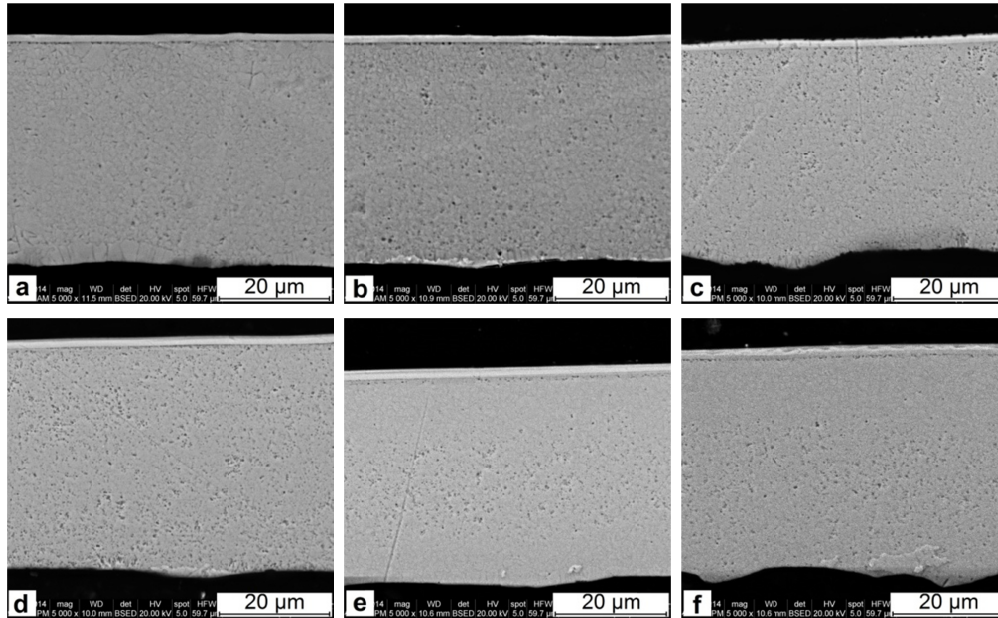


Fig. 4. The cross-section of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy ribbon irradiated with the different number of laser radiation pulses: 1 (a), 5 (b), 10 (c), 30 (d), 50 (e) and 100 (f).

In addition, the increase in the thickness of the modified layer which, by realization of the TWSME, acts as an elastic element in structural composite (Fig. 1c), at a moderate number of pulses (up to 10), results, apparently, in the increase both of the angles θ_{\max} and θ_{\min} , and $\Delta\theta$ (Fig. 2). However, at the greater number of pulses the thickness of the modified layer becomes so large, that, on the one hand, facilitates nearly full unbending of the sample with the cooling (the angle θ_{\max} is close to 180 degrees), on the other, initiates an appreciable failure to recovery of the shape by the heating (a rapid increase of the angle θ_{\min}). This leads to the decrease of the angle $\Delta\theta$ and, therefore, the magnitude of the TWSME.

The ability of the obtained samples to perform a reversible bending deformation can be used to create a variety of micromechanical devices on the basis of SME alloys, in particular microtweezers for the grip of microobjects.

4. Conclusion

The work was devoted to research into the effect of pulsed laser radiation ($\lambda = 248 \text{ nm}$, $\tau = 20 \text{ ns}$) on structural and thermomechanical properties of the rapidly quenched $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy. The number of pulses was varied from 1 to 100 at the pulse repetition rate 20 Hz and the fixed pulse energy density 17 mJ/mm^2 .

It is shown that the proposed method of laser processing the crystalline ribbons of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy in the local area leads to the formation of the TWSME. It has been established that with the increase of the number of laser radiation pulses from 1 to 10 the magnitude of the reversible angular displacement increases from 66 to 90 degrees, at the same time a further growth of the number of pulses to 100 leads to its decrease to 51 degrees.

The investigation into the structure of irradiated ribbons with the aid of X-ray structural analysis and scanning electron microscopy revealed that with the increase in the number of laser radiation pulses the thickness of the modified layer increases and the intensity of the peaks of the X-ray reflection corresponding to the martensite B19-phase decreases due to the partial amorphization.

Acknowledgements

The work was performed with the financial support of the Russian Science Foundation under grant No14-22-00098.

References

- Bellouard, Y., 2008. Shape memory alloys for microsystems: A review from a material research perspective. *Mater. Sci. Eng. A* 481-482, 582-589.
- Birnbaum, A., Satoh, G., Yao, Y., 2009. Functionally grading the shape memory response in NiTi films: Laser irradiation. *J. Appl. Phys.* 106, 043504.
- Chang, S., Wu, S., Kimura, H., 2007. Annealing effects on the crystallization and shape memory effect of Ti₅₀Ni₂₅Cu₂₅ melt-spun ribbons. *Intermetallics* 15, 233-240.
- Freed, Y., Aboudi, J., 2009. Micromechanical prediction of the two-way shape memory effect in shape memory alloy composites. *Int. J. Solids Struct.* 46, 1634-1647.
- Fu, Q., Luo, J., Flewitt, A., Ong, S., Zhang, S., 2007. Microactuators of free-standing TiNiCu films. *Smart Mater. Struct.* 16, 2651-2657.
- Gill, J., Ho, K., Carman, G., 2002. Three-dimensional thin-film shape-memory alloy micro-actuator with two-way effect. *J. MEMS* 11, 68-77.
- Glezer, A., 2012. Creation principles of new-generation multifunctional structural materials. *Physics-Uspekhi* 55(5), 522-529.
- Hartl, D., Lagoudas D., 2007. Aerospace applications of shape memory alloys. *Proc. Inst. Mech. Eng. Part G: J. Aerospace Eng.* 221, 535-552.
- Irzhak, A., Zakharov, D., Koledov, V. et al., 2014. Development of laminated nanocomposites on the bases of magnetic and non-magnetic shape memory alloys: towards new tools for nanotechnology. *J. Alloys Compd.* 586, S464-S468.
- Lagrange, T., Gotthardt, R., 2003. Microstructural evolution and thermo-mechanical response of Ni ion irradiated TiNi SMA thin films. *J. Optoelectr. Adv. Mater.* 5(1), 313-318.
- Matveeva, N., Pushin, V., Shelyakov, A., Bykovsky, Yu., Volkova, S., Kraposhin, V., 1997. Influence of crystallization conditions on structure and shape memory effects in amorphous alloys of tni-ticu system. *Fizika Metallov i Metallovedenie* 83(6), 626-632.
- Menushenkov, A., Grishina, O., Shelyakov, A. et al., 2014. Local atomic and crystal structure rearrangement during the martensitic transformation in Ti₅₀Ni₂₅Cu₂₅ shape memory alloy. *J. Alloys Compd.* 585, 428-433.
- Morgiel, J., Cesari, E., Pons, J., Pasko, A., Dutkiewicz, J., 2002. Microstructure and martensite transformation in aged Ti-25Ni-25Cu shape memory melt spun ribbons. *J. Mater. Sci.* 37, 5319-5327.
- Nespoli, A., Besseghini, S., Pittaccio, S., Villa, E., Viscuso, S., 2010. The high potential of shape memory alloys in developing miniature mechanical devices: A review on shape memory alloy mini-actuators. *Sens. Actuator A* 158, 149-160.
- Park, S., Oh, J., Kim, Y., Nam, T., 2006. Microstructures and mechanical properties of Ti-25Ni-25Cu (at.%) alloy ribbons. *Mater. Sci. Eng. A* 438-440, 695-698.
- Petrini, L., Migliavacca F., 2011. Biomedical applications of shape memory alloys. *J. Metall.* 2011, 501483.
- Potapov, P., Kulkova, S., Shelyakov, A., Okutsu, K., Miyazaki, S., Schryvers, D., 2003. Crystal structure of orthorhombic martensite in TiNi-Cu and TiNi-Pd intermetallics. *J. Phys. IV France* 112, 727-730.
- Rösner, H., Shelyakov, A., Glezer, A., Feit, K., Schlossmacher, P., 1999. A study of an amorphous-crystalline structured Ti-25Ni-25Cu (at.%) shape memory alloy. *Mater. Sci. Eng. A* 273-275, 733-737.
- Shelyakov, A., Bykovsky, Yu., Matveeva, N., Kovneristy, Yu., 1995. Formation of two-way shape memory effect in rapid-quenched TiNiCu alloys. *J. de Phys.IV. Coll.C8* 5, 713-716.
- Shelyakov, A., Larin, S., Ivanov, V., Sokolovski, V., 2003. Recent progress in the application of SMA thin ribbons for fire/heat sensing. *J. Phys. IV France* 112, 1169-1172.
- Shelyakov, A., Sitnikov, N., Koledov, V., Kuchin, D., Irzhak, A., Tabachkova, N., 2011. Melt-spun thin ribbons of shape memory TiNiCu alloy for micromechanical applications. *Int. J. of Smart and Nano Mater.* 2(2), 68-77.
- Shelyakov A., Sitnikov, N., Menushenkov, A., Koledov, V., Irjak, A., 2011. Nanostructured thin ribbons of shape memory TiNiCu alloy. *Thin Solid Films* 519, 5314-5317.
- Shelyakov, A., Sitnikov, N., Menushenkov, A., Korneev, A., Sokolova, N., 2013. Fabrication and characterization of amorphous-crystalline TiNiCu melt-spun ribbons. *J. Alloys Compd.* 577, S251-S254.
- Shelyakov, A., Sitnikov, N., Saakyan, S., Menushenkov, A., Rizakhanov, R., Korneev, A., 2013. Study of two-way shape memory behavior of amorphous-crystalline TiNiCu melt-spun ribbons. *Materials Science Forum* 738-739, 352-356.
- Sun, L., Huang, W., Ding, Z., Zhao, Y., Wang, C., Purnawali, H., Tang, C., 2012. Stimulus responsive shape memory materials: a review. *Mater. Des.* 33, 577-640.
- Van Humbeeck, J., 1999. Non-medical applications of shape memory alloys. *Mater. Sci. Eng. A* 273-275, 134-148.
- Wang, X., Bellouard, Y., Vlassak, J., 2005. Laser annealing of amorphous NiTi shape memory alloy thin films to locally induce shape memory properties. *Acta Mater.* 53, 4955-4961.
- Zakharov, D., Lebedev, G., Koledov, V. et al., 2010. An enhanced composite scheme of shape memory actuator for smart systems. *Physics Procedia* 10, 58-64.